PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Assistant Commissioner for Patents
United States Patent and Trademark Office
Box PCT
Washington, D.C.20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 29 August 2000 (29.08.00)	
International application No. PCT/SE99/02300	**Applicant's or agent's file reference** PCT 51259 si
International filing date (day/month/year) 08 December 1999 (08.12.99)	**Priority date** (day/month/year) 11 December 1998 (11.12.98)
Applicant DAHLBÄCK, Mats et al	

1. The designated Office is hereby notified of its election made:

   [X] in the demand filed with the International Preliminary Examining Authority on:

   07 July 2000 (07.07.00)

   [ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

   [ ] was not

   made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

Manu Berrod

Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

PCT

INTERNATIONAL-TYPE SEARCH REPORT

(PCT Article 15.5)

National application No.	Country or Office of filing	Applicant's or agent's file reference
9804292-2	SE	SE 400 036 OF

Filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
11 December 1998	

Applicant

Asea Brown Boveri AB

Date of request for international-type search	International-type search request No.
11 December 1998	SE 98/01421

This international-type search report has been prepared by this International Searching Authority and is transmitted to the applicant.

This international-type search report consists of a total of 2 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. [ ] **Certain claims were found unsearchable (See Box I).**

2. [ ] **Unity of invention is lacking (See Box II).**

3. [ ] The international application contains disclosure of a nucleotide and/or amino acid sequence listing and the international-type search was carried out on the basis of the sequence listing

   - [ ] filed with the international application.
   - [ ] furnished by the applicant separately from the international application,
     - [ ] but not accompanied by a statement to the effect that it did not include matter going beyond the disclosure in the international application as filed.
   - [ ] transcribed by this Authority.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
PCT 51259 si/ak		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/SE99/02300	08.12.1999	11.12.1998
International Patent Classification (IPC) or national classification and IPC7		
C 22 C 16/00, G 21 C 3/02		
Applicant		
ABB Atom AB et al		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 4 sheets, including this cover sheet.

   ☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of _____ sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
07.07.2000	30.11.2000
Name and mailing address of the IPEA/SE Patent- och registreringsverket Box 5055 S-102 42 STOCKHOLM Telex 17978 PATOREG-S Facsimile No. 08-667 72 88	Authorized officer Nils Engnell/Els Telephone No. 08-782 25 00

Form PCT/IPEA/409 (cover sheet) (January 1998)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/SE99/02300

I. Basis of the report

1. With regard to the **elements** of the international application:*

☒ the international application as originally filed

☐ the description:
pages _____, as originally filed
pages _____, filed with the letter of _____, filed with the demand
pages _____

☐ the claims:
pages _____, as originally filed
pages _____, as amended (together with any statement) under article 19
pages _____, filed with the letter of _____, filed with the demand
pages _____

☐ the drawings:
pages _____, as originally filed
pages _____, filed with the letter of _____, filed with the demand
pages _____

☐ the sequence listing part of the description:
pages _____, as originally filed
pages _____, filed with the letter of _____, filed with the demand
pages _____

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language _____ which is:

☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

☐ the language of publication of the international application (under Rule 48.3(b)).

☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☐ The amendments have resulted in the cancellation of:

☐ the description, pages _____

☐ the claims, Nos. _____

☐ the drawings, sheet/fig _____

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2 (c)).**

* *Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).*

** *Any replacement sheet containing such amendments must be referred to under item I and annexed to this report.*

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/SE99/02300

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	1-12	YES
	Claims		NO
Inventive step (IS)	Claims	1-12	YES
	Claims		NO
Industrial applicability (IA)	Claims	1-12	YES
	Claims		NO

2. Citations and explanations (Rule 70.7)

The Invention

The invention relates to a zirconium alloy for uses in nuclear plants. The main alloying elements are Nb 0.5-1.6%, Sn 0.5-0.85% and Fe 0.3-0.6%. Optionally, the alloy contains Ni <0.2% and Cr <0.6%. The alloy is optimised with respect to physical, mechanical and corrosion properties.

Documents cited in the International Search Report.

D1 US 5 560 790 A
D2 WO 94/14 990 A1
D3 Isobe T. et.al. "Development of Highly Corrosion Resistant Zirconium-Base Alloys", ASTM Publication STP 1132, Zirconium in the Nuclear Industry: Ninth International Symposium, Philadelphia 1991, pp. 246-367. p. 348-p. 353, p. 361-p. 366.

Discussion

The documents were cited to define the general state of the art not considered to be of particular relevance.

In D1 a zirconium alloy comprising Nb 0.5-2.0%, Sn 0.7-1.5% and at least one of Fe, Ni and Cr 0.07-0.28% is referred to as state of the art that. This alloy has not satisfactory corrosion properties, not even with a content of 0.3-0.6% Fe (col. 2, l 12 -. col. 3, l 21). This later composition includes the alloy according to present claims. The alloy disclosed in D1 comprises Nb 0.5-1.5%, Sn 0.9-1.5% and Fe 0.3-0.6% (col. 4, l 13-l 67). The present alloy differs from this

.../...

Supplemental Box
(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: V

in that the content of Sn is reduced. In D1 the examples indicate that increasing Sn contents increase the corrosion resistance.

D2 discloses a zirconium alloy comprising Sn 0.45-0.75%, Fe 0.4-0-53, Cr 0.2-0.3% and Nb 0.3-0.5%. It is stated that the relatively low contents of Sn and Nb improve the corrosion resistance, (p 6, l 16- p 7, l 5 and p 8 ll. 7-20). This is contradictory to what is stated in D1.

In the paper D3 the effects of Nb, Sn and Fe on strength and corrosion properties of zirconium alloys are discussed. From fig 2 and 3 it can be concluded that for contents of Nb according to the present claims the content of Sn should be low with regard to corrosion properties. However, the mechanical properties are degraded (p. 353 and p. 358 "Conclusions"). The specific alloy compositions tested according to the diagrams all contain 0.2% Fe, but can be increased to improve the tensile strength without affecting the corrosion resistance.

Conclusion

Therefore, the alloy according to present claims is novel. The statements in D1, D2 and D3 about effects, especially combined effects, of the alloying elements do not clearly indicate that the selected contents of the alloying elements in the present alloy is optimal. Consequently, the alloy according to present claims is not considered to be obvious to a person skilled in the art.

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference *(if desired) (12 characters maximum)* PCT 51259 si/cg

Box No. I TITLE OF INVENTION

"Zirconium based alloy and component in a nuclear energy plant"

Box No. II APPLICANT

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

ABB AB
SE-721 83 Västerås
SWEDEN

☐ This person is also inventor.

Telephone No.

Facsimile No.

Teleprinter No.

State *(that is, country)* of nationality: Sweden

State *(that is, country)* of residence: Sweden

This person is applicant for the purposes of: ☐ all designated States ☒ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

DAHLBÄCK, Mats
Mangelgatan 13
SE-724 76 Västerås
SWEDEN

This person is:

☐ applicant only

☒ applicant and inventor

☐ inventor only *(If this check-box is marked, do not fill in below.)*

State *(that is, country)* of nationality: Sweden

State *(that is, country)* of residence: Sweden

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

☒ Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: ☒ agent ☐ common representative

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

BJERKÉNS PATENTBYRÅ KB, represented by
BERGLUND, Stefan; ISRAELSSON, Stefan;
BJERKÉN, Håkan; FRÖDERBERG, Oskar; or
OLSSON, Jan;
Östermalmsgatan 58
SE-114 50 Stockholm, SWEDEN

Telephone No. 08 - 662 08 70

Facsimile No. 08 - 663 02 60

Teleprinter No.

☐ **Address for correspondence:** Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

If none of the following sub-boxes is used, this sheet should not be included in the request.

Name and address: *(Family name followed by given name: for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

LIMBÄCK, Magnus
Släggargatan 16
SE-723 37 Västerås
SWEDEN

This person is:
- ☐ applicant only
- ☒ applicant and inventor
- ☐ inventor only *(If this check-box is marked, do not fill in below.)*

State *(that is, country)* of nationality: Sweden

State *(that is, country)* of residence: Sweden

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: *(Family name followed by given name: for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

WIKMARK, Gunnar
Oslogatan 49
SE-752 34 Uppsala
SWEDEN

This person is:
- ☐ applicant only
- ☒ applicant and inventor
- ☐ inventor only *(If this check-box is marked, do not fill in below.)*

State *(that is, country)* of nationality: Sweden

State *(that is, country)* of residence: Sweden

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: *(Family name followed by given name: for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

This person is:
- ☐ applicant only
- ☐ applicant and inventor
- ☐ inventor only *(If this check-box is marked, do not fill in below.)*

State *(that is, country)* of nationality:

State *(that is, country)* of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: *(Family name followed by given name: for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

This person is:
- ☐ applicant only
- ☐ applicant and inventor
- ☐ inventor only *(If this check-box is marked, do not fill in below.)*

State *(that is, country)* of nationality:

State *(that is, country)* of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.

Box No.V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) *(mark the applicable check-boxes: at least one must be marked)*:

Regional Patent

- ☐ AP **ARIPO Patent:** GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SZ Swaziland, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☐ EA **Eurasian Patent:** AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ EP **European Patent:** AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☐ OA **OAPI Patent:** BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT *(if other kind of protection or treatment desired, specify on dotted line)* .....

National Patent *(if other kind of protection or treatment desired, specify on dotted line)*:

- ☐ AL Albania
- ☐ AM Armenia
- ☐ AT Austria and utility model
- ☐ AU Australia
- ☐ AZ Azerbaijan
- ☐ BA Bosnia and Herzegovina
- ☐ BB Barbados
- ☐ BG Bulgaria
- ☐ BR Brazil
- ☐ BY Belarus
- ☒ CA Canada
- ☐ CH and LI Switzerland and Liechtenstein
- ☐ CN China
- ☐ CU Cuba
- ☐ CZ Czech Republic and utility model
- ☐ DE Germany and utility model
- ☐ DK Denmark and utility model
- ☐ EE Estonia and utility model
- ☐ ES Spain
- ☐ FI Finland and utility model
- ☐ GB United Kingdom
- ☐ GE Georgia
- ☐ GH Ghana
- ☐ GM Gambia
- ☐ GW Guinea-Bissau
- ☐ HR Croatia
- ☐ HU Hungary
- ☐ ID Indonesia
- ☐ IL Israel
- ☐ IS Iceland
- ☒ JP Japan
- ☐ KE Kenya
- ☐ KG Kyrgyzstan
- ☐ KP Democratic People's Republic of Korea
- ☐ KR Republic of Korea
- ☐ KZ Kazakhstan
- ☐ LC Saint Lucia
- ☐ LK Sri Lanka
- ☐ LR Liberia
- ☐ LS Lesotho
- ☐ LT Lithuania
- ☐ LU Luxembourg
- ☐ LV Latvia
- ☐ MD Republic of Moldova
- ☐ MG Madagascar
- ☐ MK The former Yugoslav Republic of Macedonia
- ☐ MN Mongolia
- ☐ MW Malawi
- ☐ MX Mexico
- ☐ NO Norway
- ☐ NZ New Zealand
- ☐ PL Poland
- ☐ PT Portugal
- ☐ RO Romania
- ☐ RU Russian Federation
- ☐ SD Sudan
- ☐ SE Sweden
- ☐ SG Singapore
- ☐ SI Slovenia
- ☐ SK Slovakia and utility model
- ☐ SL Sierra Leone
- ☐ TJ Tajikistan
- ☐ TM Turkmenistan
- ☐ TR Turkey
- ☐ TT Trinidad and Tobago
- ☐ UA Ukraine
- ☐ UG Uganda
- ☒ US United States of America
- ☐ UZ Uzbekistan
- ☐ VN Viet Nam
- ☐ YU Yugoslavia
- ☐ ZW Zimbabwe

Check-boxes reserved for designating States (for the purposes of a national patent) which have become party to the PCT after issuance of this sheet:

- ☐ .....
- ☐ .....

Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. *(Confirmation of a designation consists of the filing of a notice specifying that designation and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 15-month time limit.)*

Box No. VI PRIORITY CLAIM ☐ Further priority claims are indicated in the Supplemental Box.

Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is: national application: country	regional application:* regional Office	international application: receiving Office
item (1) 11/12/1998	9804292-2	Sweden		
item (2)				
item (3)				

☒ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) *(only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office)* identified above as item(s): (1)

* *Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.*

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) *(if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used)*: ISA / SE

Request to use results of earlier search; reference to that search *(if an earlier search has been carried out by or requested from the International Searching Authority)*:

Date (day/month/year)	Number	Country (or regional Office)
02/07/1999	SE98/01421	Sweden

Box No. VIII CHECK LIST: LANGUAGE OF FILING

This international application contains the following **number of sheets**:

request	:	4
description (excluding sequence listing part)	:	9
claims	:	2
abstract	:	1
drawings	:	
sequence listing part of description	:	
Total number of sheets	:	16

This international application is **accompanied by** the item(s) marked below:

1. ☒ fee calculation sheet
2. ☐ separate signed power of attorney
3. ☐ copy of general power of attorney; reference number, if any:
4. ☐ statement explaining lack of signature
5. ☐ priority document(s) identified in Box No. VI as item(s):
6. ☐ translation of international application into (language):
7. ☐ separate indications concerning deposited microorganism or other biological material
8. ☐ nucleotide and/or amino acid sequence listing in computer readable form
9. ☒ other *(specify)*: ITS-report

Figure of the drawings which should accompany the abstract: —

Language of filing of the international application: Swedish

Box No. IX SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

Stockholm, 7 December 1999
BJERKÉNS PATENTBYRÅ KB

Stefan Israelsson

For receiving Office use only

1. Date of actual receipt of the purported international application:	2. Drawings: ☐ received: ☐ not received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:	
4. Date of timely receipt of the required corrections under PCT Article 11(2):	
5. International Searching Authority (if two or more are competent): ISA /	6. ☐ Transmittal of search copy delayed until search fee is paid.

For International Bureau use only

Date of receipt of the record copy by the International Bureau:

This sheet is not part of and does not count as a sheet of the international application.

PCT

FEE CALCULATION SHEET

Annex to the Request

For receiving Office use only

International application No.

Date stamp of the receiving Office

Applicant's or agent's file reference: PCT 51259 si/cg

Applicant: ABB AB et al

CALCULATION OF PRESCRIBED FEES

1. TRANSMITTAL FEE . . . . . 1 000:- T

2. SEARCH FEE . . . . . 8 510:- S

International search to be carried out by _____

(If two or more International Searching Authorities are competent in relation to the international application, indicate the name of the Authority which is chosen to carry out the international search.)

3. INTERNATIONAL FEE

Basic Fee

The international application contains 16 sheets.

first 30 sheets 3 500:- b1

_____ (remaining sheets) x _____ (additional amount) = _____ b2

Add amounts entered at b1 and b2 and enter total at B . . . . 3 500:- B

Designation Fees

The international application contains 4 designations.

4 (number of designation fees payable *(maximum 10)*) x 800:- (amount of designation fee) = 3 200:- D

Add amounts entered at B and D and enter total at I . . . . . 6 700:- I

(Applicants from certain States are entitled to a reduction of 75% of the international fee. Where the applicant is (or all applicants are) so entitled, the total to be entered at I is 25% of the sum of the amounts entered at B and D.)

4. FEE FOR PRIORITY DOCUMENT *(if applicable)* . . . . . P

5. TOTAL FEES PAYABLE . . . . . 16 210:- TOTAL

Add amounts entered at T, S, I and P, and enter total in the TOTAL box

☐ The designation fees are not paid at this time.

MODE OF PAYMENT

☐ authorization to charge deposit account (see below)	☐ bank draft	☐ coupons
☒ cheque	☐ cash	☐ other *(specify)*:
☐ postal money order	☐ revenue stamps	

DEPOSIT ACCOUNT AUTHORIZATION *(this mode of payment may not be available at all receiving Offices)*

The RO/ _____

☐ is hereby authorized to charge the total fees indicated above to my deposit account.

☐ *(this check-box may be marked only if the conditions for deposit accounts of the receiving Office so permit)* is hereby authorized to charge any deficiency or credit any overpayment in the total fees indicated above to my deposit account.

☐ is hereby authorized to charge the fee for preparation and transmittal of the priority document to the International Bureau of WIPO to my deposit account.

Deposit Account No. _____ Date *(day/month/year)* _____ Signature _____

The demand must be filed directly with the competent International Preliminary Examining Authority if two or more Authorities are competent. with the one chosen by the applicant. The full name or two-letter code of that Authority may be indicated by the applicant on the line below:

IPEA/ SE

PCT

CHAPTER II

DEMAND

under Article 31 of the Patent Cooperation Treaty:

The undersigned requests that the international application specified below be the subject of international preliminary examination according to the Patent Cooperation Treaty and hereby elects all eligible States (except where otherwise indicated).

For International Preliminary Examining Authority use only

Identification of IPEA

Date of receipt of DEMAND

Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION

Applicant's or agent's file reference: PCT 51259 si/ak

International application No.: PCT/SE99/02300

International filing date *(day/month/year)*: 8/12/99

(Earliest) Priority date *(day/month/year)*: 11/12/98

Title of invention: "Zirconium based alloy and component in a nuclear energy plant"

Box No. II APPLICANT(S)

Name and address: *(Family name followed by given name: for a legal entity, full official designation. The address must include postal code and name of country.)*

ABB Atom AB
SE-721 63 Västerås
Sweden

Telephone No.:

Facsimile No.:

Teleprinter No.:

State *(that is, country)* of nationality: Sweden

State *(that is, country)* of residence: Sweden

Name and address: *(Family name followed by given name: for a legal entity, full official designation. The address must include postal code and name of country.)*

DAHLBÄCK, Mats
Mangelgatan 13
SE-724 76 Västerås
Sweden

State *(that is, country)* of nationality: Sweden

State *(that is, country)* of residence: Sweden

Name and address: *(Family name followed by given name: for a legal entity, full official designation. The address must include postal code and name of country.)*

State *(that is, country)* of nationality:

State *(that is, country)* of residence:

[X] Further applicants are indicated on a continuation sheet.

See Notes to the demand form

Sheet No. 2

International application No.
PCT/SE99/02300

Continuation of Box No. II APPLICANT(S)

If none of the following sub-boxes is used, this sheet should not be included in the demand.

Name and address: *(Family name followed by given name: for a legal entity, full official designation. The address must include postal code and name of country.)*

LIMBÄCK, Magnus
Släggargatan 16
SE-723 37 Västerås
Sweden

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☐ Further applicants are indicated on another continuation sheet.

International application No.
PCT/SE99/02300

Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The following person is [X] agent [ ] common representative

and [X] has been appointed earlier and represents the applicant(s) also for international preliminary examination.

[ ] is hereby appointed and any earlier appointment of (an) agent(s)/common representative is hereby revoked.

[ ] is hereby appointed, specifically for the procedure before the International Preliminary Examining Authority, in addition to the agent(s)/common representative appointed earlier.

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

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[ ] **Address for correspondence:** Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Box No. IV BASIS FOR INTERNATIONAL PRELIMINARY EXAMINATION

Statement concerning amendments:*

1. The applicant wishes the international preliminary examination **to start on the basis of:**

[X] the international application as originally filed

the description [ ] as originally filed
[ ] as amended under Article 34

the claims [ ] as originally filed
[ ] as amended under Article 19 (together with any accompanying statement)
[ ] as amended under Article 34

the drawings [ ] as originally filed
[ ] as amended under Article 34

2. [ ] The applicant wishes any amendment to the claims under Article 19 to be considered as reversed.

3. [ ] The applicant wishes the start of the international preliminary examination **to be postponed** until the expiration of 20 months from the priority date unless the International Preliminary Examining Authority receives a copy of any amendments made under Article 19 or a notice from the applicant that he does not wish to make such amendments (Rule 69.1(d)). *(This check-box may be marked only where the time limit under Article 19 has not yet expired.)*

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Language for the purposes of international preliminary examination: English

[ ] which is the language in which the international application was filed.

[X] which is the language of a translation furnished for the purposes of international search.

[X] which is the language of publication of the international application.

[ ] which is the language of the translation (to be) furnished for the purposes of international preliminary examination.

Box No. V ELECTION OF STATES

The applicant hereby **elects all eligible States** *(that is, all States which have been designated and which are bound by Chapter II of the PCT)*

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Sheet No. 4

International application No.
PCT/SE99/02300

Box No. VI CHECK LIST

The demand is accompanied by the following elements, in the language referred to in Box No. IV, for the purposes of international preliminary examination:			For International Preliminary Examining Authority use only: received	not received
1. translation of international application	:	sheets	☐	☐
2. amendments under Article 34	:	sheets	☐	☐
3. copy (or, where required, translation) of amendments under Article 19	:	sheets	☐	☐
4. copy (or, where required, translation) of statement under Article 19	:	sheets	☐	☐
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6. other *(specify)*	:	sheets	☐	☐

The demand is also accompanied by the item(s) marked below:

1. [X] fee calculation sheet
2. [ ] separate signed power of attorney
3. [ ] copy of general power of attorney; reference number, if any:
4. [ ] statement explaining lack of signature
5. [ ] nucleotide and or amino acid sequence listing in computer readable form
6. [ ] other *(specify)*:

Box No. VII SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the demand).

Stockholm, 5 July, 2000
Bjerkéns Patentbyrå KB

Stefan Israelsson

For International Preliminary Examining Authority use only

1. Date of actual receipt of DEMAND:
2. Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b):
3. ☐ The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and item 4 or 5. below, does not apply. ☐ The applicant has been informed accordingly.
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Demand received from IPEA on:

CHAPTER II

PCT

FEE CALCULATION SHEET

Annex to the Demand for international preliminary examination

International application No. PCT/SE99/02300	For International Preliminary Examining Authority use only
Applicant's or agent's file reference PCT 51259 si/ak	Date stamp of the IPEA
Applicant: ABB Atom AB et al	

Calculation of prescribed fees

1. Preliminary examination fee	4 200:- P	
2. Handling fee *(Applicants from certain States are entitled to a reduction of 75% of the handling fee. Where the applicant is (or all applicants are) so entitled, the amount to be entered at H is 25% of the handling fee.)*	1 270:- H	
3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box	5 470:- TOTAL	

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See Notes to the fee calculation sheet

PCT

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(74) Agents: BERGLUND, Stefan et al.; Bjerkéns Patentbyrå KB, Östermalmsgatan 58, S-114 50 Stockholm (SE).

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(54) Title: ZIRCONIUM BASED ALLOY AND COMPONENT IN A NUCLEAR ENERGY PLANT

(57) Abstract

A zirconium-based alloy, suitable for use in a corrosive environment, where it is subjected to increased radiation and comprises 0.5-1.6 percentage by weight Nb and 0.3-0.6 percentage by weight Fe. The alloy is characterised in that it comprises 0.5-0.85 percentage by weight Sn.

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Zirconium-based alloy and component in a nuclear energy plant

BACKGROUND OF THE INVENTION AND PRIOR ART

The present invention concerns a zirconium-based alloy, suitable for use in a corrosive environment where it is subjected to increased radiation and comprising 0.5-1.6 percentage by weight Nb and 0.3-0.6 percentage by weight Fe. The invention also concerns a component in a nuclear energy plant, which comprises an alloy of the mentioned kind.

According to the prior art it is known to provide, in a nuclear energy plant, a component which comprises a zirconium-based alloy of the above-mentioned kind. Such an alloy has the advantage of fulfilling the requirements which are demanded on mechanical as well as corrosion properties of a material which in a corrosive environment is subjected to an increased radiation, in particular neutron radiation of the fast neutron kind.

Thanks to its relatively high Fe-content it is possible through a suitable heat treatment, comprising annealing and quenching, to obtain secondary phase particles consisting of Zr, Fe and Nb in a matrix of α-phase of the zirconium-based alloy. By a suitable choice of the heat treatment variables time and temperature it is furthermore, with given contents of the included alloying materials Nb and Fe, possible to control the size of and the distribution of the secondary phase particles. The secondary phase particles may have a positive effect on the corrosion resistance of the alloy. It is therefore important to optimize the distribution of and

the size of the existing secondary phase particles. It is thereby highly important to find a suitable composition of the alloying elements included in the alloy.

The document US 5 560 790 describes a zirconium-based alloy which comprises 0.5-1.5 percentage by weight Nb, 0.9-1.5 percentage by weight Sn and 0.3-0.6 percentage by weight Fe. Furthermore, this alloy comprises 0.005-0.2 percentage by weight Cr, 0.005-0.04 percentage by weight C, 0.05-0.15 percentage by weight O, 0.005-0.15 percentage by weight Si and the rest Zr. Thereby a microstructure is achieved in the material which includes particles of the kind $Zr(Nb,Fe)_2$, $Zr(Nb,Cr,Fe)$ and $(Zr,Nb)_3Fe$. These secondary phase particles give the material good corrosion properties and good mechanical properties. Thanks to the high Fe-content, precipations of β-Nb-phase are avoided, which would have a negative influence on the resistance of the material against local corrosion attacks.

Sn is said to have a high solubility in the α-phase and will therefore, when it is present to the given amount, be dissolved in the α-phase and contribute to improved corrosion properties and mechanical properties of the same. It is pointed out that a too low content of Sn (below 0.9 percentage by weight) in the material influences the tensile strength of the material both in the long and in the short term. Furthermore, such a low Sn-content suppresses to a smaller extent a negative effect of a possible nitrogen incorporation on the corrosion resistance of the material. A Sn content above 1.5 percentage by weight influences the susceptibility of the material to working and in particular to cold working.

It is mentioned that Si and C contribute to a reduction of the size of the particles and to bring about a structural homogeneity in the material.

Oxygen is said to contribute to a finer structure of the material and is also used as a means for reinforcing the material through the solid solution, a so-called "solid solution strengthener".

Nb is said to contribute to the strength properties of Zr and increases the corrosion resistance of the alloy by forming secondary phase particles together with Zr and Fe.

It is furthermore pointed out that with a Nb-content below 0.5 percentage by weight of the material, a Fe-content below 0.3 percentage by weight and a Cr-content below 0.005 percentage by weight, the total portion of secondary phase particles of the above-mentioned kind in the α-zirconium matrix of the end product is considerably lower than 60 percentage by volume of the total amount of iron-containing secondary phase particles, which results in that the corrosion resistance of the material is negatively influenced. With a Nb-content above 1.5 percentage by weight, a large number of large particles of β-Nb phase are formed in the material, which also reduces the corrosion resistance of the same.

It is also mentioned that a Cr-content above 0.2 percentage by weight may result in the formation of binary intermetallic compounds of Zr-Cr, which has an opposite i.e. negative, influence on the workability and the tensile strength of the material.

SUMMARY OF THE INVENTION

A purpose with the present invention is to provide a zirconium-based alloy with such a composition that the distribution of and the size of secondary phase particles in the alloy, the kind of secondary phase particles and the

content of different alloying elements in the α-phase of the alloy are such that the alloy is optimized with respect to physical and mechanical properties as well as corrosion properties. In particular, these properties should be optimized with respect to an application where the alloy is subjected to an increased radiation of the fast-neutron kind in a corrosive environment, such as in the reactor core of a nuclear energy plant. In particular it is aimed at improved corrosion properties of the alloy with respect to the corrosion properties of the above-mentioned alloys according to the prior art.

This purpose is achieved by means of an alloy of the kind initially defined, which alloy is characterised in that it comprises 0.5-0.85 percentage by weight Sn. This choice of Sn-content stands in opposition to that which, according to the prior art, is a preferred interval for the Sn-content. The applicant has however found that improved corrosion properties, in particular in the environment which is the case in the area of the reactor core of a nuclear energy plant, may be achieved in the zirconium-based alloy by a careful choice of the Sn-content within the defined interval.

According to a preferred embodiment of the alloy, the content of Sn in the alloy is larger than or equal to 0.65 percentage by weight. A preferred interval for the Sn-content should thus be 0.65-0.85 percentage by weight with the purpose of achieving as good corrosion properties in the alloy as possible under the otherwise given conditions.

According to a further preferred embodiment, the alloy comprises up to 0.2 percentage by weight Ni. Thereby secondary phase particles containing Zr, Ni and Fe may be obtained in the alloy. Such secondary phase particles

contribute to improved corrosion properties of the alloy and have good stability under neutron radiation.

According to a further preferred embodiment, the alloy comprises up to 0.6 percentage by weight Cr, which is more than the maximum 0.2 percentage by weight which has previously been recommended with respect to the formation of binary intermetallic compounds of Cr and Zr. With the remaining composition which the alloy according to the invention has, a content of up to 0.6 percentage by weight Cr may however be permitted in order to improve the corrosion properties of the alloy, without the alloy thereby obtaining considerably worse mechanical properties, such as a deteriorated tensile strength. Unlike the prior art, the present invention thus suggests a zirconium-based alloy with a Cr-content above 0.2 percentage by weight, up to 0.6 percentage by weight.

According to a further preferred embodiment, the total content of Nb and Sn is larger than or equal to 1.15 percentage by weight. Such a total content of Nb and Sn contributes to improved mechanical properties of the alloy.

Which requirements on mechanical properties and corrosion properties that finally are demanded on the alloy depend on in which application the alloy finally is to be used. According to a preferred embodiment of the invention, the alloy constitutes at least a part of a component in a nuclear energy plant. The component is preferably arranged in the area of the reactor core and constitutes, according to a further preferred embodiment, a part of a fuel assembly. In such an application high requirements will at least be demanded on the corrosion properties of the alloy. Depending on to which extent the component has a supporting function, specific requirements will also be demanded on the mechanical properties of the alloy. An alloy of the kind

which is suggested by the invention is in particular suitable to constitute at least a part of a cladding tube, a spacer or a box.

A further purpose of the invention is to provide a component in a nuclear energy plant, which component in particular has satisfactory corrosion properties with respect to the specific conditions which may be assumed to be the case in the nuclear energy plant, in particular in the area of the core of the same, where the component is subjected to an increased radiation of the fast neutron kind, in a corrosive environment, e.g. surrounded by a corrosive medium, such as water.

This purpose is achieved by means of a component of the initially defined kind, which comprises an alloy according to the invention.

According to a preferred embodiment, the component constitutes a part of a fuel assembly, i.e. it is arranged in the area of the reactor core. Thereby specific requirements are demanded on its corrosion properties in the environment of increased radiation and corrosive media which it is subjected to. The choice of a zirconium-base alloy with a suitable composition is consequently highly important.

According to a further preferred embodiment, the component defines a cladding tube. Thereby also specific mechanical properties of the component are required, which are fulfilled by the alloy according to the invention.

According to a further preferred embodiment, at least a part of the inner circumference of the cladding tube comprises a layer of a material which is more ductile than the alloy according to the invention. The cladding tube is thereby

made less sensitive to the direct contact with the fuel within these. The risk for crack formation of the cladding tube in areas where it comes into direct contact with and possibly is subjected to wear caused by the fuel is reduced, under the condition that the layer of the more ductile material is arranged in these areas, which preferably is the case. Said layer comprises here a zirconium-based alloy with a total content of alloying materials which does not exceed 0.5 percentage by weight.

Further advantages with and features of the alloy according to the invention and the component, respectively, will be clear from the following, detailed description.

DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT

A component arranged in a nuclear energy plant, more precisely in the area of the reactor core, is subjected to increased radiation of the fast neutron kind in a corrosive environment. The reactor may be a pressure water or a boiling water reactor. The component constitutes a part of the fuel assembly. In this example the component is a cladding tube arranged to contain the reactor fuel.

The component comprises a zirconium-based alloy which has the following composition:

0.5-0.85 percentage by weight Sn,
0.3-0.6 percentage by weight Fe,
0-0.6 percentage by weight Cr,
0-0.2 percentage by weight Ni,
0.65-1.6 percentage by weight Nb and the rest zirconium.

The content of Ni is preferably within the interval 0.05-0.2 percentage by weight.

According to an alternative embodiment the alloy comprises
0.65-0.85 percentage by weight Sn and
0.5-1.6 percentage by weight Nb,
with the remaining elements within the previously mentioned intervals.

The cladding tube may be formed from a solid bar, in the centre of which a hole has been drilled. Furthermore, the component has, in addition to prior annealings in connection with the working of the same, finally been annealed in the β-phase area of the alloy and then been quenched by a β-quenching in the α-phase area of the alloy.

By the annealing in the β-phase area, course structures and other effects of the prior heat treatment history are removed from the alloy. Furthermore, the orientated texture which has been obtained during prior working of the work piece of the tube is removed, whereby different tendencies to growth in different directions of the component, when it is exposed to neutron radiation in the core, are avoided.

The cooling to the α-phase area is so fast that an entity of short α-phase laminae is formed in the prior β-phase grains. Short α-laminae improve the mechanical strength of the alloy.

Furthermore at the quenching from the β-phase area to the α-phase area secondary phase particles of intermetallic compounds, such as $Zr(Nb,Fe)_2$, $Zr(Fe,Cr,Nb)$ and $(Zr,Nb)_3Fe$, are precipitated, which favours good anticorrosive and mechanical properties of the finished alloy and thereby of the component. The quenching speed should thereby be adjusted such that an optimal secondary phase particle distribution and secondary phase average particle size are obtained. The alloy is preferably cooled with a cooling

speed below 100°C/second, preferably below 50°C/second and most preferred in order of magnitude 5-20°C/second.

When the component, such as here, is a cladding tube, preferably a layer with a lower total content of alloying elements than the remaining alloy is applied on the inner circumference of the cladding tube. The total content of alloying materials in this layer is preferably below 0.5 percentage by weight, wherein the remaining part constitutes Zr. This layer makes the cladding tube more resistant to mechanical influence from the reactor fuel which is arranged in the tube and which physically may rest against and cause tensions in the walls of the cladding tube.

Preferably the alloy according to the invention comprises no essential amount of other materials than those which have been mentioned above. It should however be noted that small amounts of impurities may exist in the alloy. Typical impurities which may exist in zirconium-based alloys are specified in the table below. Furthermore, small amounts of Si and O may exist in the alloy. Typical contents of these materials are also given below:

Table:

Element	Al	B	C	Ca	Cd	Cl	Co
Max.ppm	75	0.5	270	30	0.5	20	20

Element	Cu	H	Hf	Mg	Mn	Mo	N
Max.ppm	50	25	100	20	50	50	80

Element	Na	Pb	Si	Ti	U
Max.ppm	20	130	120	50	3.5

Si and O may exist in contents where Si is 50-120 ppm and O is 500-1600 ppm.

It should be realised that a number of alternative embodiments of the alloy and the component according to the invention will be obvious to a person skilled in the art but still be within the scope of the invention, such as it is defined in the annexed claims.

Claims

1. A zirconium-based alloy, suitable for use in a corrosive environment, where it is subjected to increased radiation, wherein the alloy, in addition to zirconium and for zirconium of a reactor quality normal contents of impurities, comprises 0.5-1.6 percentage by weight Nb and 0.3-0.6 percentage by weight Fe, characterised in that it comprises 0.5-0.85 percentage by weight Sn.

2. A zirconium-based alloy according to claim 1, characterised in that the content of Sn in the alloy is larger than or equal to 0.65 percentage by weight.

3. A zirconium-based alloy according to claim 1 or 2, characterised in that it comprises up to 0.2 percentage by weight Ni.

4. A zirconium-based alloy according to any one of the claims 1-3, characterised in that it comprises up to 0.6 percentage by weight Cr.

5. A zirconium-based alloy according to any one of the claims 1-4, characterised in that the total content of Nb and Sn is larger than or equal to 1.15 percentage by weight.

6. A zirconium-based alloy according to any one of the claims 1-5, characterised in that the alloy constitutes at least a part of a component in a nuclear energy plant.

7. A zirconium-based alloy according to claim 6, characterised in that said component constitutes a part of a fuel assembly.

8. A component in a nuclear energy plant, characterised in that it comprises an alloy according to any one of the claims 1-5.

9. A component according to claim 8, characterised in that it constitutes a part of a fuel assembly.

10. A component according to claim 8 or 9, characterised in that it defines a cladding tube for nuclear fuel.

11. A component according to claim 10, characterised in that at least a part of the inner circumference of the component comprises a layer of a material which is more ductile than said alloy.

12. A component according to claim 11, characterised in that said layer comprises a zirconium-based alloy with a total content of alloying elements which does not exceed 0.5 percentage by weight.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 99/02300

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C22C 16/00, G21C 3/02
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, METADEX, PASCAL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Zirconium in the Nuclear Industry: Ninth International Symposium, Volume, 1991, (Philadelphia), Isobe T. et al, "Development of Highly Corrosion Resistant Zirconium-Base Alloys, ASTM Publication STP 1132", page 246 - page 367, see page 348-350, 353,358; figures 2,3 --	1-12
A	US 5560790 A (ANTONINA V. NIKULINA ET AL), 1 October 1996 (01.10.96), column 2, line 12 - column 3, line 21; column 4, line 13 - line 67 --	1-12
A	WO 9414990 A1 (COMBUSTION ENGINEERING, INC.), 7 July 1994 (07.07.94), page 5, line 5 - page 8, line 20 --	1-12

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
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Date of the actual completion of the international search	Date of mailing of the international search report
15 March 2000	19 -04- 2000
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Nils Engnell/MP Telephone No. +46 8 782 25 00

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/SE 99/02300

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5560790 A	01/10/96	AU 7670394 A	24/10/94
		DE 59307895 D	00/00/00
		EP 0643144 A,B	15/03/95
		SE 0643144 T3	
		RU 2032759 C	10/04/95
		WO 9423081 A	13/10/94
		RU 2032760 C	10/04/95
		JP 8502099 T	05/03/96
WO 9414990 A1	07/07/94	AU 4805993 A	19/07/94
		US 5254308 A	19/10/93

Zirkoniumbaserad legering och komponent i en kärnenergianläggning

UPPFINNINGENS BAKGRUND OCH TIDIGARE TEKNIK

Föreliggande uppfinning avser en zirkoniumbaserad legering, lämpad för användning i en korrosiv miljö där den är föremål för förhöjd strålning och innefattande 0,5-1,6 viktsprocent Nb och 0,3-0,6 viktsprocent Fe. Uppfinningen avser dessutom en komponent i en kärnenergianläggning, vilken innefattar en legering av det nämnda slaget.

Enligt tidigare teknik är det känt att i en kärnenergianläggning anordna en komponent som innefattar en zirkoniumbaserad legering av det ovan nämnda slaget. En sådan legering har fördelen att uppfylla de krav som ställs på såväl mekaniska egenskaper som korrosionsegenskaper hos ett material som i en korrosiv miljö är föremål för en förhöjd strålning, i synnerhet neutronstrålning av typen snabba neutroner.

Tack vare dess relativt höga Fe-innehåll är det möjligt att genom lämplig värmebehandling, innefattande glödgning och snabbkylning, erhålla sekundärfaspartiklar bestående av Zr, Fe och Nb hos en matris av α-fas hos den zirkoniumbaserade legeringen. Genom lämpligt val av värmebehandlingsvariablerna tid och temperatur är det dessutom, med givna halter av de ingående legeringsämnena Nb och Fe, möjligt att styra storleken på och fördelningen av sekundärfaspartiklarna. Sekundärfaspartiklarna kan ha en positiv effekt på legeringens korrosionshärdighet. Det är därför viktigt att optimera fördelningen av och storleken på de förekommande sekundärfaspartiklarna. Det är därvid av yttersta vikt

att finna en lämplig sammansättning av de i legeringen ingående legeringselementen.

Skriften US 5,560,790 beskriver en zirkoniumbaserad legering som innefattar 0,5-1,5 viktsprocent Nb, 0,9-1,5 viktsprocent Sn och 0,3-0,6 viktsprocent Fe. Dessutom innehåller denna legering 0,005-0,2 viktsprocent Cr, 0,005-0,04 viktsprocent C, 0,05-0,15 viktsprocent O, 0,005-0,15 viktsprocent Si och resten Zr. Därigenom uppnås en mikrostruktur hos materialet som inbegriper partiklar av typen $Zr(Nb,Fe)_2$, Zr(Nb,Cr,Fe) och $(Zr,Nb)_3Fe$. Dessa sekundärfaspartiklar förlänar materialet goda korrosionsegenskaper och goda mekaniska egenskaper. Tack vare den höga Fe-halten undviks utskiljningar av β-Nb-fas, vilka skulle ha en negativ inverkan på materialets motståndskraft mot lokala korrosionsangrepp.

Sn sägs ha hög löslighet i α-fasen och kommer därför, då det är närvarande i den givna mängden, att vara inlöst i α-fasen och bidra till förbättrade korrosionsegenskaper och mekaniska egenskaper hos denna. Det framhålls att ett alltför lågt innehåll av Sn (under 0,9 viktsprocent) hos materialet påverkar brotthållfastheten både på lång och kort sikt hos detta. Dessutom undertrycker ett sådant lågt Sn-innehåll i mindre utsträckning en negativ effekt av eventuell kväveinblandning på materialets korrosionshållfasthet. Ett Sn-innehåll över 1,5 viktsprocent påverkar materialets mottaglighet för bearbetning och i synnerhet kallbearbetning.

Det nämns att Si och C bidrar till att reducera storleken på partiklar och tillföra strukturhomogenitet hos materialet.

Syre sägs bidra till en finare struktur hos materialet och används även som ett medel för att förstärka materialet genom den fasta lösningen, en så kallad "solid solution strengthener".

Nb sägs bidra till hållfasthetsegenskaperna hos Zr och ökar legeringens korrosionshållfasthet genom att bilda sekundärfaspartiklar tillsammans med Zr och Fe.

Det konstateras vidare att med ett Nb-innehåll under 0,5 viktsprocent hos materialet, ett Fe-innehåll under 0,3 viktsprocent och ett Cr-innehåll under 0,005 viktsprocent, är den totala andelen av sekundärfaspartiklar av det ovan nämnda slaget i α-zirkoniummatrisen hos slutprodukten väsentligt lägre än 60 volymprocent av den totala mängden av järnhaltiga sekundärfaspartiklar, vilket resulterar i att korrosionshållfastheten hos materialet påverkas negativt. Med ett Nb-innehåll över 1,5 viktsprocent, bildas ett stort antal stora partiklar av β-Nb-fas i materialet, vilket också reducerar dettas korrosionsresistans.

Det nämns också att ett Cr-innehåll över 0,2 viktsprocent kan resultera i bildande av binära intermetalliska föreningar av Zr-Cr, vilket har motsatt, d.v.s. negativ inverkan på bearbetbarheten och brotthållfastheten hos materialet.

SAMMANFATTNING AV UPPFINNINGEN

Ett syfte med den föreliggande uppfinningen är att tillhandahålla en zirkoniumbaserad legering med en sådan sammansättning att fördelningen av och storleken på sekundärfaspartiklar i legeringen, typen av sekundärfaspartiklar och innehållet av olika legeringselement i legeringens α-fas är sådana att legeringen är optimerad med hänsyn till såväl fysikaliska och mekaniska egenskaper som korrosionsegenskaper. I synnerhet skall dessa egenskaper vara optimerade med hänsyn till en tillämpning där legeringen är föremål för förhöjd strålning av typen snabba neutroner i en korrosiv miljö, såsom i reaktorhärden hos en kärnenergianläggning. I synnerhet eftersträvas förbättrade korrosionsegenskaper hos legeringen i förhållande till korrosionsegenskaperna hos de ovan nämnda legeringarna enligt tidigare teknik.

Detta syfte uppnås medelst en legering av det inledningsvis definierade slaget, vilken är kännetecknad av att den innefattar 0,5-0,85 viktsprocent Sn. Detta val av Sn-innehåll står i motsägelse till vad som, enligt tidigare teknik, är ett föredraget intervall för Sn-innehållet. Sökanden har emellertid kunnat konstatera att förbättrade korrosionsegenskaper, i synnerhet i den miljö som uppträder i området av reaktorhärden hos en kärnenergianläggning, kan uppnås hos den zirkoniumbaserade legeringen genom ett omsorgsfullt val av Sn-innehåll inom det definierade intervallet.

Enligt ett föredraget utförande av legeringen är innehållet av Sn i legeringen större än eller lika med 0,65 viktsprocent. Ett föredraget intervall för Sn-innehållet torde sålunda vara 0,65-0,85 viktsprocent i syfte att uppnå så goda korrosionsegenskaper hos legeringen som möjligt under de i övrigt givna förutsättningarna.

Enligt ytterligare ett föredraget utförande innefattar legeringen upp till 0,2 viktsprocent Ni. Därigenom kan sekundärfaspartiklar innehållande Zr, Ni och Fe erhållas i legeringen. Sådana sekundärfaspartiklar bidrar till förbättrade korrosionsegenskaper hos legeringen och har god stabilitet under neutronbestrålning.

Enligt ytterligare ett föredraget utförande innefattar legeringen upp till 0,6 viktsprocent Cr, vilket är mer än de maximala 0,2 viktsprocent som tidigare rekommenderats med hänsyn till bildandet av binära intermetalliska föreningar av Cr och Zr. Med den sammansättning som den uppfinningsenliga legeringen i övrigt uppvisar kan ett innehåll av upp till 0,6 viktsprocent Cr emellertid tillåtas för att förbättra korrosionsegenskaperna hos legeringen, utan att legeringen därvid erhåller remarkabelt försämrade mekaniska egenskaper, såsom försämrad brotthållfasthet. Till skillnad från tidigare teknik föreslår sålunda den föreliggande uppfinningen en zirkoniumbaserad legering med ett Cr-innehåll över 0,2 viktsprocent, ända upp till 0,6 viktsprocent.

Enligt ytterligare ett föredraget utförande är det totala innehållet av Nb och Sn större än eller lika med 1,15 viktsprocent. Ett så-

dant totalt innehåll av Nb och Sn bidrar till förbättrade mekaniska egenskaper hos legeringen.

Vilka krav på mekaniska egenskaper och korrosionsegenskaper som slutligen ställs på legeringen beror av i vilken applikation legeringen till sist skall användas. Enligt ett föredraget utförande av uppfinningen bildar legeringen åtminstone en del av en komponent i en kärnenergianläggning. Komponenten är företrädesvis anordnad i området av reaktorhärden och bildar, enligt ett ytterligare föredraget utförande, del av en bränslepatron. I en sådan applikation kommer stora krav att åtminstone ställas på legeringens korrosionsegenskaper. Beroende av i vilken utsträckning komponenten har en bärande funktion kommer också specifika krav att ställas på legeringens mekaniska egenskaper. En legering av det slag som föreslås av uppfinningen är i synnerhet lämpad att utgöra åtminstone en del av ett kapslingsrör, en spridare eller en box.

Ett ytterligare syfte med uppfinningen är att tillhandahålla en komponent i en kärnenergianläggning, vilken komponent i synnerhet uppvisar tillfredsställande korrosionsegenskaper med hänsyn till de specifika förhållanden som kan antas föreligga i kärnenergianläggningen, i synnerhet i området av dennas härd, där komponenten är föremål för förhöjd strålning av typen snabba neutroner, i en korrosiv miljö, t ex omgiven av ett korrosivt medium, såsom vatten.

Detta syfte uppnås medelst en komponent av det inledningsvis definierade slaget, vilken innefattar en legering av det uppfinningsenliga slaget.

Enligt ett föredraget utförande bildar komponenten del av en bränslepatron, d.v.s den är anordnad i området av reaktorhärden. Därvid ställs speciella krav på dess korrosionsegenskaper i den miljö av förhöjd strålning och korrosiva media som den är föremål för. Valet av en zirkoniumbaserad legering med lämplig sammansättning är följaktligen av yttersta vikt.

Enligt ytterligare ett föredraget utförande definierar komponenten ett kapslingsrör. Därvid fordras även specifika mekaniska egenskaper hos komponenten, vilka uppfylls av den uppfinningsenliga legeringen.

Enligt ytterligare ett föredraget utförande innefattar åtminstone en del av kapslingsröret inre omfång ett skikt av ett mer duktilt material än den uppfinningsenliga legeringen. Därigenom görs kapslingsröret mindre känsligt för den direkta kontakten med bränslet inuti dessa. Risken för sprickbildning hos kapslingsröret i områden där denna kommer i direkt kontakt med och eventuellt är föremål nötning på grund av bränslet reduceras, under förutsättning att skiktet av det mer duktila materialet är anordnat i dessa områden, vilket företrädesvis är fallet. Nämnda skikt innefattar här en zirkoniumbaserad legering med en total halt av legeringsämnen som icke överstiger 0,5 viktsprocent.

Ytterligare fördelar med och särdrag hos den uppfinningsenliga legeringen respektive komponenten kommer att framgå av den följande, detaljerade beskrivningen.

DETALJERAD BESKRIVNING AV ETT FÖREDRAGET UTFÖRANDE

En komponent anordnad i en kärnenergianläggning, närmare bestämt i området av reaktorhärden, är föremål för förhöjd strålning av typen snabba neutroner i en korrosiv miljö. Reaktorn kan vara en tryckvatten- eller en kokarvattenreaktor. Komponenten bildar del av bränslepatronen. I detta exempel är komponenten ett kapslingsrör inrättat att inhysa reaktorbränslet.

Komponenten innefattar en zirkoniumbaserad legering vilken har följande sammansättning:

0,5-0,85 viktsprocent Sn,
0,3-0,6 viktsprocent Fe,
0-0,6 viktsprocent Cr,
0-0,2 viktsprocent Ni,
0,65-1,6 viktsprocent Nb och resten zirkonium.

Innehållet av Ni ligger företrädesvis i intervallet 0,05-0,2 viktsprocent.

Enligt ett alternativt utförande innefattar legeringen
0,65-0,85 viktsprocent Sn och
0,5-1,6 viktsprocent Nb,
med övriga element inom de tidigare nämnda intervallen.

Kapslingsröret kan vara bildat utifrån en solid stång, i vars centrum ett hål borrats. Vidare har komponenten, förutom tidigare glödgningar i samband med bearbetningen därav, slutligen glödgats i legeringens β-fasområde och sedan snabbkylts genom en β-släckning till legeringens α-fasområde.

Genom glödgningen i β-fasområdet avlägsnas grova strukturer och andra effekter av tidigare värmebehandlingshistorik ur legeringen. Dessutom avlägsnas den orienterade textur som erhållits vid tidigare bearbetningar av rörämnet, varigenom olika benägenhet till växning i olika riktningar hos komponenten, då denna utsätts för neutronstrålningen i härden, undviks.

Kylningen till α-fasområdet är så snabb att paket av korta α-faslameller bildas i de tidigare β-faskornen. Korta α-lameller gynnar legeringens mekaniska hållfasthet.

Vid snabbkylningen från β-fasområdet till α-fasområdet utskiljs dessutom sekundärfaspartiklar av intermetalliska föreningar, såsom $Zr(Nb,Fe)_2$, $Zr(Fe,Cr,Nb)$ och $(Zr,Nb)_3Fe$, vilka gynnar goda

antikorrosiva och mekaniska egenskaper hos den färdiga legeringen och därmed komponenten. Kylningshastigheten bör därvid anpassas så att en optimal sekundärfaspartikelfördelning och sekundärfaspartikelmedelstorlek erhålls. Legeringen är företrädesvis kyld med en svalningshastighet under 100°C/sekund, företrädesvis under 50°C/sekund och helst i storleksordningen 5-20°C/-sekund.

Då komponenten, såsom här, är ett kapslingsrör, är företrädesvis ett skikt med lägre total halt av legeringselement än hos legeringen i övrigt applicerad på kapslingsrörets inneromfång. Den totala halten av legeringsämnen hos detta skikt ligger företrädesvis under 0,5 viktsprocent, varvid återstoden utgörs av Zr. Detta skikt gör kapslingsröret mer motståndskraftigt mot mekanisk påverkan från det reaktorbränsle som är anordnat i röret och som fysiskt kan komma att ligga an mot och orsaka spänningar i kapslingsrörets väggar.

Företrädesvis innefattar legeringen enligt uppfinningen ingen väsentlig mängd av andra ämnen än de som omnämnts ovan. Det ska emellertid noteras att små mängder föroreningar kan finnas i legeringen. Typiska föroreningar som förekommer i zirkoniumbaserade legeringar är specificerade i tabellen nedan. Dessutom kan små mängder av Si och O förekomma i legeringen. Typiska halter av dessa ämnen anges också nedan.

Tabell:

Element	Al	B	C	Ca	Cd	Cl	Co
Max.ppm	75	0,5	270	30	0,5	20	20

Element	Cu	H	Hf	Mg	Mn	Mo	N
Max.ppm	50	25	100	20	50	50	80

Element	Na	Pb	Si	Ti	U
Max.ppm	20	130	120	50	3,5

Si och O förekommer i halter där Si är 50 -120 ppm och O är 500 – 1600 ppm.

Det skall inses att en rad alternativa utföranden av den uppfinningsenliga legeringen och komponenten kommer att vara uppenbara för en fackman inom området men ändock ligga inom ramen för uppfinningen, såsom den är definierad i de bifogade patentkraven.

Krav

1. Zirkoniumbaserad legering, lämpad för användning i en korrosiv miljö, där den är föremål för förhöjd strålning, varvid legeringen, förutom zirkonium och för zirkonium av reaktorkvalitet normala halter av föroreningar, innefattar 0,5-1,6 viktsprocent Nb och 0,3-0,6 viktsprocent Fe, kännetecknad av att den innefattar 0,5-0,85 viktsprocent Sn.

2. Zirkoniumbaserad legering enligt krav 1, kännetecknad av att innehållet av Sn i legeringen är större än eller lika med 0,65 viktsprocent.

3. Zirkoniumbaserad legering enligt krav 1 eller 2, kännetecknad av att den innefattar upp till 0,2 viktsprocent Ni.

4. Zirkoniumbaserad legering enligt något av kraven 1-3, kännetecknad av att den innefattar upp till 0,6 viktsprocent Cr.

5. Zirkoniumbaserad legering enligt något av kraven 1-4, kännetecknad av att det totala innehållet av Nb och Sn är större än eller lika med 1,15 viktsprocent.

6. Zirkoniumbaserad legering enligt något av kraven 1-5, kännetecknad av att legeringen bildar åtminstone en del av en komponent i en kärnenergianläggning.

7. Zirkoniumbaserad legering enligt krav 6, kännetecknad av att nämnda komponent bildar del av en bränslepatron.

8. Komponent i en kärnenergianläggning, kännetecknad av att den innefattar en legering enligt något av kraven 1-5.

9. Komponent enligt krav 8, kännetecknad av att den bildar del av en bränslepatron.

10. Komponent enligt krav 8 eller 9, kännetecknad av att den definierar ett kapslingsrör för kärnbränsle.

11. Komponent enligt krav 10, kännetecknad av att åtminstone en del av dess inneromfång innefattar ett skikt av ett material som är mer duktilt än nämnda legering.

12. Komponent enligt krav 11, kännetecknad av att nämnda skikt innefattar en zirkoniumbaserad legering med en total halt av legeringsämnen icke överstigande 0,5 viktsprocent.

Sammandrag

En zirkoniumbaserad legering, lämpad för användning i en korrosiv miljö, där den är föremål för förhöjd strålning och innefattande 0,5-1,6 viktsprocent Nb och 0,3-0,6 viktsprocent Fe. Legeringen är kännetecknad av att den innefattar 0,5-0,85 viktsprocent Sn.